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Influence of a modulated surface on the properties of liquid-liquid interfaces

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We present an extension to the linear Gouy-Chapman theory for an interface between two immiscible electrolytes (ITIES) with an interface that deviates from a planar geometry. This theory takes into account the proper boundary condition for an ITIES, i.e., neither the potential nor the surface charge is fixed at the boundary between the electrolytes. Instead, the dielectric displacement at the interface position is allowed to respond to the perturbation from a flat surface. The linear and quadratic response functions are calculated self-consistently. We derive a roughness function in terms of a height-height correlation function of the surface, which determines the behavior of the capacity and the free energy of a modulated ITIES. Furthermore, we calculate the appropriate electrostatic contribution to the elastic bending modulus of the interface. [S1063-651X(98)10410-5]

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I. INTRODUCTION

In recent years liquid-liquid interfaces have received great attention because they play an important role in biological, chemical, and physical systems. For instance, in biology they can serve as a model for membranes separating two electrolytes and in chemistry they are important for reactions involving ion transfer across an interface. Since in many respects the interface between two immiscible electrolyte solutions (ITIES) shows an analogy to the metal-solution interface, they have also attracted the interest of electrochemists.

There have been a considerable number of experimental investigations using classical electrochemical techniques such as voltammetry and electrochemical impedance [1]. Recently, also more modern techniques such as second harmonic generation [2] have been applied to these systems. However, in spite of these efforts, and in contrast to metal-solution interfaces, only little is known about the structure of liquid-liquid interfaces. One point of view is that the solvents form a sharp boundary and a compact layer of solvent molecules, which the ions cannot penetrate [3]. The other view claims the existence of a mixed layer of the solutions [4]. On the other hand, there are strong hints that the interfacial structure of liquid-liquid interfaces is different from metal-solution interfaces, in the absence of specific adsorption. So the measured capacity at low electrolyte concentrations is found to be higher than the Gouy-Chapman capacity [1,5], while at metal electrodes it is lower.

In contrast with experimental investigations, there have been only relatively few theoretical investigations of liquid-liquid interfaces and they also provide no unique picture of the interfacial structure. Computer simulations of these systems [6,7] show that there is a sharp interface at which the two liquids do not mix, whereas recent calculations based on the density functional formalism predict a mixed solvent layer [8]. This is also confirmed within a simple lattice gas model [9]. Including ions in this approach, it was also possible to explain the higher capacity compared to the Gouy-Chapman capacity by the existence of a mixed boundary layer, whose thickness extends over several solvent diameters [5]. Of course, the extent of this boundary layer depends on the solubility of one solvent in the other. Hence the different results need not be contradictory, but are due to the solvent parameters used in the calculations.

So far the theoretical investigations of ITIES have been restricted to a planar geometry of the interface. In this work we will follow another line and investigate the effect of modulated interface geometries. The interface between two liquid phases is not planar, but roughened due to thermal fluctuations of the interface position. The size of this effect is mainly determined by the surface tension of the system. Molecular dynamics simulations of an interface between water and 1,2 DCE [6] have shown that the structure of the interface can be described within the theory of capillary waves [10,11]. If one neglects the effects of gravitation, the mean square height fluctuation of the surface in Fourier space is given by

$$\langle \hat{h}^2(\mathbf{q}) \rangle = \frac{k_B T}{\gamma q^2}, \tag{1}$$

where $\hat{h}(\mathbf{q})$ is the Fourier transform of the function describing the surface modulation, $\mathbf{q}$ is the wave vector, and γ is the surface tension. Since the surface tension for liquid-liquid interfaces is much lower than for metal-solution interfaces (e.g., 30 dyn/cm for the 1,2 DCE–water interface [12] and 415 dyn/cm for the Hg-water interface [13]), the thermal excitation of these fluctuations can be quite important. From statistical mechanics of membranes [13] it is also well known that there is another kind of fluctuation that is governed by the elastic bending modulus k_c of the membrane if the surface tension is small. For this type of fluctuation the mean height fluctuation is given by

$$\langle \hat{h}^2(\mathbf{q}) \rangle = \frac{k_B T}{k_c q^4}. \tag{2}$$

For long wavelengths these *curvature fluctuations* are lower in energy ($\sim q^4$) than the *surface-tension fluctuations*

($\sim q^2$) and they are therefore expected to be even more important for the modulation of the surface.

This short discussion shows that for ITIES it is natural to consider an interface that is perturbed from a flat geometry. In this work we will assume that the interface position can be described by a given height function $h(x,y)$, which is mainly determined by the properties of the interface between the two pure solvents. Furthermore, we will focus only on an ideally polarizable interface and neglect the effects of specific adsorption or ion association. Having this kind of system in mind, we will derive an extension to the linear Gouy-Chapman theory, which takes into account the modulated geometry of the interface. We are aware of the much more elaborate theories of electric double layers [14], which go far beyond the mean-field level of the Gouy-Chapman theory, taking into account many microscopic details of the system. However, all these theories deal with highly symmetric geometries such as planes, cylinders, and spheres. Therefore, it should be of basic interest to investigate the effect of modulated surfaces on the interfacial properties within a simple theory in order to understand some main physical aspects, at least on a qualitative level. By main physical aspects we mean the interplay between the two Debye lengths of the system and the two new length scales introduced by the surface modulation, namely, the height of the modulation and its characteristic length, e.g., the wavelength in the case of a periodic surface. Moreover, the Gouy-Chapman theory is by far the most used theory for the classification of experimental results and the linearized version should give a reasonable description for low potential drops across the interface.

The approach we used in this work is similar to that of Goldstein *et al.* [15], who considered an interface between a modulated surface on one side and an electrolyte solution on the other. The same technique was later used by Daikhin *et al.* [16] in order to discuss the capacity at a rough metal-solution interface. In the case of ITIES, however, the boundary conditions used by Goldstein *et al.* [15] are inappropriate, and one has to employ a much more complicated one. This will be developed in Sec. II, where we describe the theoretical method for the solution of the linear Poisson-Boltzmann equation and calculate the two-dimensional potential profile. In Sec. III we calculate the capacity for the modulated liquid-liquid interface and compare it to the Gouy-Chapman result for the flat interface. We also give an explicit example for a simple deterministic height function and discuss the results for different parameters. In Sec. IV we investigate the influence of the curvature on the free energy of the system and derive the appropriate expression for the electrostatic contribution to the elastic bending modulus. Finally, we give a short summary and an outlook in Sec. V.

II. THEORETICAL APPROACH

As already mentioned in the Introduction, we have to deal with a boundary value problem for a complicated geometry. In order to simplify the calculations, we consider only a two-dimensional system, that is, the surface is modulated in only one spatial direction and is translationally invariant along the orthogonal direction in the midplane of the surface. A two-dimensional modulation of the surface can introduce some additional features due to the possible change of the topology of the surface. The investigation of these effects may be the topic of future work, but we think that the main aspects can be understood also from a more simple one-dimensional model of the surface modulation.

A. Boundary condition

The mathematical problem in the spirit of the Gouy-Chapman theory can be stated as follows. We have to solve the two-dimensional linearized Poisson-Boltzmann equation

$$(\partial_{xx}+\partial_{yy}-\kappa_i^2)V(x,y)=c_i, \tag{3}$$

where c_i is a constant, which is usually set to zero on one side. For a 1-1 binary electrolyte the inverse Debye length is $\kappa_i=\lambda_{DB}^{-1}=\sqrt{\rho_{Bi}e^2/\epsilon_i k_B T}$, where ρ_{Bi} is the total ionic density in the bulk of the solution i, $\epsilon_i=\epsilon_{solv,i}\epsilon_0$ is the solvent dielectric constant, and $i=1$ for $y>h(x)$ and $i=2$ for $y<h(x)$. The potential $V(x,y)$ is the total potential of the system, but image effects due to the different dielectric constants are not contained. The height function $h(x)$ describes the modulation of the boundary between the two solutions and is assumed to be known. Furthermore, we assume that

$$\int_{-\infty}^{+\infty} h(x)=0. \tag{4}$$

This can always be achieved by a suitable choice of the midplane position. If we consider the flat surface as the reference system, that is, the spontaneous curvature of the surface is zero, this assumption entails no loss of generality.

In order to solve this second-order partial differential equation we need two boundary conditions. Consider first the case of a metal-solution interface, where the metal on side 2 $[y<h(x)]$ is assumed to behave ideally. Then Eq. (3) has to be solved only for the half space $y>h(x)$ with the Dirichlet boundary conditions

$$V(x,y=h(x))=V_0\equiv\text{const},\quad V(x,\infty)=c_1\equiv 0. \tag{5}$$

This problem was solved by Goldstein *et al.* [15]. They also solved the problem for a Neumann boundary condition at the interface:

$$[-\mathbf{n}(x)\boldsymbol{\nabla}V(x,y)]_{y=h(x)}=\sigma_0\equiv\text{const},\quad V(x,\infty)=c_1\equiv 0, \tag{6}$$

where $\mathbf{n}(x)$ is the normal vector pointing from the interface towards side 1. Both cases correspond to the situation where the reference electrode far from the interface is a flat equipotential line, i.e., it does not follow the modulation of the interface. This is the usual electrochemical setup for measuring or imposing a potential drop across the interface. It is well known, but we stress it here again that for a flat surface both types of boundary conditions yield the same potential profile (and also for other highly symmetric geometries such as spheres and cylinders). However, this is not the case for an arbitrary surface and we will see that this leads to important differences in the electrical and thermodynamic properties of modulated double layers.

In the case of an ITIES, where neither of the two sides behaves as an ideal conductor, the boundary condition is more complicated since the potential drop occurs on both sides of the interface and the boundary is surely not an equipotential line. Furthermore, it is also not valid to use two independent Neumann boundary conditions for each side since the interface between two immiscible solutions is electrically transparent. Only in the case of totally absorbing interfaces, which screen side 1 from side 2, would this be the appropriate boundary condition.

It is important to emphasize that the quantity that can be independently controlled in an experiment is the total potential drop ΔV across the interface. This means that one has no direct influence on the interface position itself. So the appropriate boundary condition for an overall neutral ITIES is simply

$$V(x,-\infty)=c_2\equiv\Delta V,\quad V(x,\infty)=c_1\equiv 0. \tag{7}$$

However, from electrostatics it is known that the dielectric displacement **D** at the boundary between to different dielectric media has to fulfill the condition [17]

$$\mathbf{n}(x)[\mathbf{D}_1(x,y=h(x))-\mathbf{D}_2(x,y=h(x))]=\sigma(x), \tag{8}$$

where $\sigma(x)$ is the surface charge density on the interface. The application of this condition to our problem requires some further discussion. The first important point to note is that $\sigma(x)$ is really a *singular* quantity located at $y=h(x)$. Since in this work we will restrict ourselves to the case where we have no nonelectrostatic adsorption of ionic species at the interface, the surface charge density $\sigma(x)$ is zero and the normal component of the dielectric displacement is continuous at the interface:

$$\mathbf{n}(x)\mathbf{D}_1(x,y=h(x))=\mathbf{n}(x)\mathbf{D}_2(x,y=h(x)). \tag{9}$$

Second, it is important to realize that the continuity of the dielectric displacement is only a *local* condition, as indicated by the x dependence. Indeed, for a liquid-liquid interface, which on the Gouy-Chapman level is treated as point ions in a dielectric continuum, the charges can move freely and respond to the modulation of the surface in such a way that the total free energy of the interphase is minimized. It would be a gross oversimplification if we assume a constant dielectric displacement at the interface. This means that at the interface we can fix neither the dielectric displacement or the surface charge nor the potential. The behavior of $\mathbf{n}(x)\mathbf{D}(x,h(x))$ and $V(x,h(x))$ is completely determined by the potential drop ΔV imposed across the overall interface and the properties of the interface itself. Since the x dependence of the dielectric displacement is due to the deviation of the interface from a planar geometry, we can write it in the general form

$$\mathbf{n}(x)\mathbf{D}_i(x,h(x))=\sigma_i+\int dx'\,\alpha_i(x-x')h(x') + \int dx'\int dx''\beta_i(x-x',x'-x'')h(x')\times h(x'')+\cdots . \tag{10}$$

This equation describes the dielectric displacement at the boundary as a *nonlinear* and *nonlocal* response of the surface charge distribution to the perturbation $h(x)$. This can be interpreted in the following way: In the case of a modulated interface the dielectric displacement at the boundary is not simply given by the local surface charge density σ_i, but it contains additional contributions from all the other points on the surface. In order to see the first nonvanishing influence on quantities that involve an integration over the lateral dimension, we have to go to the second order in the height function because the first-order terms vanish due to the condition of Eq. (4). The constant σ_i and the nonlocal response functions α_i and β_i have to be determined self-consistently. It is convenient to solve Eq. (3) together with the boundary conditions (7) and (9) separately for $y<h(x)$ and $y>h(x)$ and require the continuity of the potential at the interface:

$$V_1(x,y=h(x))=V_2(x,y=h(x)). \tag{11}$$

With Eq. (3) and Eqs. (7)–(11) the problem is now completely defined and the response functions α and β can be determined.

B. Perturbative approach

In order to solve the linearized Poisson-Boltzmann equation [Eq. (3)] subject to the boundary conditions (7) and (10) we assume that $h(x)$ is a small quantity. In this case we can use standard perturbative techniques for solving differential equations with complicated boundaries [19,15]. There is also an approach based on the multiple scattering technique [20], which gives a formally exact solution of the linearized Poisson-Boltzmann equation. However, since in this work we introduce a boundary condition, which itself is written as a perturbative expansion in $h(x)$ [see Eq. (10)], the standard perturbative technique for the solution of Eq. (3) is more convenient. In the following we will describe the solution for side 1 and drop the corresponding index.

If we introduce a parameter of smallness λ, we can write a perturbative expansion of the dielectric displacement at the interface

$$\mathbf{D}(x,\lambda h(x))\simeq\mathbf{D}(x,0)+\lambda h(x)\mathbf{D}_y(x,0) + \frac{1}{2!}\lambda^2 h(x)^2_{yy}\mathbf{D}(x,0)+\cdots , \tag{12}$$

where the subscript indicates the differentiation. We have to write also an expansion of the normal vector since it depends on the derivative of the height function

$$\mathbf{n}(x)=\begin{pmatrix}-\lambda h_x(x)\\ 1\end{pmatrix}\frac{1}{\sqrt{1+\lambda^2 h_x^2(x)}} \simeq\begin{pmatrix}-\lambda h_x(x)\\ 1\end{pmatrix}\left(1-\frac{1}{2}\lambda^2 h_x^2(x)+\cdots\right). \tag{13}$$

Furthermore, we assume that the potential itself has the following expansion in λ:

$$V(x,y)=V^{(0)}(x,y)+\lambda V^{(1)}(x,y)+\lambda^2 V^{(2)}(x,y)+\cdots . \tag{14}$$

Substituting Eqs. (12) and (13) into Eq. (10), using $\mathbf{D}(x,y)=-\epsilon\nabla V(x,y)$, and collecting terms with the same order of λ, we obtain the hierarchy of boundary conditions for $V_y(x,0)$,

$$-V_y^{(0)}(x,0)=\frac{\sigma}{\epsilon},\tag{15a}$$

$$\begin{aligned}-V_y^{(1)}(x,0)&=h(x)V_{yy}^{(0)}(x,0)-h_x(x)V_x^{(0)}(x,0)\\&\quad+\int dx'\,\alpha(x-x')h(x'),\end{aligned}\tag{15b}$$

$$\begin{aligned}-V_y^{(2)}(x,0)&=h(x)V_{yy}^{(1)}(x,0)+\frac{1}{2!}h^2(x)V_{yyy}^{(0)}(x,0)\\&\quad-h_x(x)V_x^{(1)}(x,0)-h_x(x)h(x)V_{xy}^{(1)}(x,0)\\&\quad+\frac{1}{2}h_x^2(x)\frac{\sigma}{\epsilon}+\int dx'\int dx''\beta_i\\&\quad\times(x-x',x'-x'')h(x')h(x'').\end{aligned}\tag{15c}$$

This hierarchy looks much more complicated than Eq. (10), but now we have recast the boundary condition for a complicated surface into a series of boundary conditions for a simple planar geometry. If we now substitute Eq. (14) into Eq. (3), we see that each order of $V(x,y)$ satisfies a linear Poisson-Boltzmann equation

$$(\partial_{xx}+\partial_{yy}-\kappa^2)V^{(n)}(x,y)=0\quad\forall n.\tag{16}$$

The problem can now be solved order by order and this is most conveniently done by introducing the lateral Fourier transform of the potential

$$\hat{V}(q,y)=\int_{-\infty}^{\infty}dx\;e^{iqx}V(x,y).\tag{17}$$

Equation (16) now has the form

$$(\partial_{yy}-\kappa_q^2)\hat{V}^{(n)}(q,y)=0\quad\forall n,\tag{18}$$

where

$$\kappa_q=\kappa r_q,\quad r_q=\sqrt{1+\frac{q^2}{\kappa^2}}.\tag{19}$$

The formal solution is then

$$\hat{V}^{(n)}(q,y)=\hat{V}^{(n)}(q,0)e^{-\kappa_q y}\tag{20}$$

and each order of $\hat{V}^{(n)}(q,0)$ can be determined from the Fourier transformation of Eq. (15). The final result up to the second order in the height function can be written for each side as

$$\hat{V}_i(q,y)=\sum_n\hat{V}_i^{(n)}(q,0)\exp[(-1)^i\kappa_{i,q}y],\tag{21}$$

with

$$\hat{V}_i^{(0)}(q,0)=\pm\frac{\sigma_i}{\epsilon_i\kappa_i}2\pi\delta(q)+c_i\quad\text{with }c_1=0,\quad c_2=\Delta V\tag{22a}$$

$$\hat{V}_i^{(1)}(q,0)=\frac{1}{\epsilon_i\kappa_{i,q}}[\sigma_i\kappa_i\pm\hat{\alpha}_i(q)]\hat{h}(q),\tag{22b}$$

$$\begin{aligned}\hat{V}_i^{(2)}(q,0)&=\pm\frac{1}{\epsilon_i\kappa_{i,q}}\int\frac{dk}{2\pi}\hat{h}(q-k)\hat{h}(k)\\&\quad\times\left\{\frac{1}{2}\sigma_i\kappa_i^2\left[(2r_{i,k}-1)+\frac{(q-k)k}{\kappa_i^2}\left(\frac{2}{r_{i,k}}-1\right)\right]\right.\\&\quad\left.\pm\hat{\alpha}_i(k)\left[\kappa_{i,k}+\frac{(q-k)k}{\kappa_{i,k}}\right]+\hat{\beta}_i(q,k)\right\},\end{aligned}\tag{22c}$$

where the upper sign of ± refers to $i=1$. In order to stop this expansion at the second-order term the condition $\kappa h(x)\ll 1$ must hold. Furthermore, the height function $h(x)$ must be infinitely differentiable since otherwise the series does not converge [15]. We see that the inverse Debye length is modified by the wave vector of the modulation. Since $\kappa_q\geqslant\kappa$ the higher-order terms decay faster than the zeroth order and far from the interface we recover the usual Gouy-Chapman result.

C. Determination of the response functions α and β

Having the general form of the solution for the potential, the remaining task is now to calculate the constants σ_i and the response functions α_i and β_i. This can easily be done by satisfying the other conditions for the dielectric displacement and the potentials on sides 1 and 2. From Eq. (11), which has also to be expanded like Eq. (10), and Eq. (9) we get after some tedious algebra for each order in λ a set of two equations: for λ^0 terms

$$\begin{pmatrix}1&-1\\1/\epsilon_1\kappa_1&1/\epsilon_2\kappa_2\end{pmatrix}\begin{pmatrix}\sigma_1\\\sigma_2\end{pmatrix}=\begin{pmatrix}0\\\Delta V\end{pmatrix}\tag{23}$$

and the solution

$$\sigma_1=\sigma_2=\sigma=C_{GC}\Delta V,\tag{24}$$

with

$$C_{GC}=\left(\frac{1}{\epsilon_1\kappa_1}+\frac{1}{\epsilon_2\kappa_2}\right)^{-1};\tag{25}$$

and for λ^1 terms

$$\begin{pmatrix}1&-1\\1/\epsilon_1\kappa_{1,q}&1/\epsilon_2\kappa_{2,q}\end{pmatrix}\begin{pmatrix}\hat{\alpha}_1(q)\\\hat{\alpha}_2(q)\end{pmatrix}=\begin{pmatrix}0\\A(q)\end{pmatrix},\tag{26}$$

with

$$A(q)=\frac{\sigma_2}{\epsilon_2}\left(\frac{1}{r_{2,q}}-1\right)-\frac{\sigma_1}{\epsilon_1}\left(\frac{1}{r_{1,q}}-1\right),\tag{27}$$

and the solution

$$\hat{\alpha}_1(q)=\hat{\alpha}_2(q)=\hat{\alpha}(q)=C_{GC,q}A(q),\tag{28}$$

with

$$C_{GC,q}=\left(\frac{1}{\epsilon_1\kappa_{1,q}}+\frac{1}{\epsilon_2\kappa_{2,q}}\right)^{-1}; \tag{29}$$

and for λ^2 terms

$$\begin{pmatrix} 1 & -1 \\ 1/\epsilon_1\kappa_{1,q} & 1/\epsilon_2\kappa_{2,q} \end{pmatrix}\begin{pmatrix}\hat\beta_1(q,k)\\ \hat\beta_2(q,k)\end{pmatrix}=\begin{pmatrix}0\\ B(q,k)\end{pmatrix}, \tag{30}$$

with

$$B(q,k)=\frac{1}{2}\,\frac{\sigma_1\kappa_1}{\epsilon_1}f_1^\sigma(q,k)+\frac{1}{2}\,\frac{\sigma_2\kappa_2}{\epsilon_2}f_2^\sigma(q,k) + \frac{\hat\alpha_1(k)}{\epsilon_1}f_1^\alpha(q,k)-\frac{\hat\alpha_2(k)}{\epsilon_2}f_2^\alpha(q,k) \tag{31}$$

and

$$f_i^\sigma(q,k)=1-\frac{1}{r_{i,q}}\left\{(2r_{i,k}-1)+\frac{(q-k)k}{\kappa_i^2}\left(\frac{2}{r_{i,k}}-1\right)\right\}, \tag{32}$$

$$f_i^\alpha(q,k)=1-\frac{1}{r_{i,q}}\left\{r_{i,k}+\frac{(q-k)k}{\kappa_i^2 r_{i,k}}\right\}, \tag{33}$$

and the solution

$$\hat\beta_1(q,k)=\hat\beta_2(q,k)=\hat\beta(q,k)=C_{GC,q}B(q,k). \tag{34}$$

Inserting Eqs. (24), (28), and (34) into Eq. (21) and performing the back transformation in real space, the two-dimensional potential profile is completely determined in terms of the solution parameters ϵ_i and κ_i, the potential drop ΔV across the interface, and the height function $h(x)$.

A quantity of particular interest is the lateral potential distribution at the interface position $y=h(x)$, which we can now express through the potential on side 1:

$$\hat V(q,h(x))=\Delta V\frac{C_{GC}}{\epsilon_1\kappa_1}\left\{2\pi\delta(q)+\hat h(q)\hat F^{(1)}(q) + \int\frac{dk}{2\pi}\,\hat h(q-k)\hat h(k)\hat F^{(2)}(q,k)\right\}, \tag{35}$$

with

$$\hat F^{(1)}(q)=-f_1^\alpha(0,q)\kappa_1-\frac{C_{GC,q}}{r_{i,q}}\left[\frac{f_2^\alpha(0,q)}{\epsilon_2}-\frac{f_1^\alpha(0,q)}{\epsilon_1}\right], \tag{36}$$

$$\begin{aligned}\hat F^{(2)}(q,k)=&-\frac{1}{2}\left[\kappa_1 f_1^\sigma(q,k)-\frac{C_{GC,q}}{r_{1,q}}\left(\frac{f_1^\sigma(q,k)}{\epsilon_1}+\frac{f_2^\sigma(q,k)}{\epsilon_2}\right)\right]\\ &-C_{GC,k}\left(\frac{f_2^\alpha(0,k)}{\epsilon_2}-\frac{f_1^\alpha(0,k)}{\epsilon_1}\right)\\ &\times\left[\kappa_1 f_1^\alpha(q,k)+\frac{C_{GC,q}}{r_{1,q}}\left(\frac{f_2^\alpha(q,k)}{\epsilon_2}-\frac{f_1^\alpha(q,k)}{\epsilon_1}\right)\right].\end{aligned} \tag{37}$$

Due to the second-order contribution, the potential does not follow the modulation of the interface. This is also true for the charge density since in the linear regime the charge density is proportional to the potential.

In the limit $\epsilon_2\rightarrow\infty$, $\kappa_2\rightarrow\infty$, which corresponds to an ideal metal-solution interface, the first- and the second-order contributions go to zero and we obtain an equipotential line at the interface boundary

$$V(x,y=h(x))=\Delta V. \tag{38}$$

The constant σ and the response functions have then the form

$$\sigma=\epsilon_1\kappa_1\Delta V, \tag{39}$$

$$\hat\alpha(q)=-\kappa_1\sigma(1-r_{1,q}), \tag{40}$$

$$\hat\beta(q,k)=\frac{1}{2}\sigma\kappa_1^2 r_{1,q}f_1^\sigma(q,k)+\hat\alpha(k)\kappa_1 r_{1,q}f_1^\alpha(q,k). \tag{41}$$

If we insert Eqs. (39)–(41) into Eq. (21) we obtain the same expression for the potential as Goldstein *et al.* [15], who started from an equipotential line at the surface as the boundary condition. So our approach is a general result for the potential drop across an interface between two conducting materials, where the pure material on both sides can be described by a dielectric constant. It is therefore also applicable to the interface between the conductor and semiconductor, the semiconductor and electrolyte, or two semiconductors.

III. CAPACITY AND ROUGHNESS FUNCTION

One easily accessible experimental quantity is the differential capacity C of an ITIES, which is defined as [21]

$$C=\frac{dQ}{d(\Delta V)}. \tag{42}$$

Here Q is the total interfacial excess charge on one side of the interface. The total charge on each side is given by

$$Q_1=\int dx\int_{h(x)}^{\infty}dy\;\rho_1(x,y),\quad Q_2=\int dx\int_{-\infty}^{h(x)}dy\;\rho_2(x,y). \tag{43}$$

Since in the linearized Poisson-Boltzmann approximation the charge density distribution is proportional to the potential, $\rho(x,y)=-\epsilon\kappa^2V(x,y)$ [if $V(x,\pm\infty)=0$], we can calculate the charge very easily. The result up to second order in the height function is

$$-Q_1\equiv Q_2=Q=\sigma A_{\mathrm{real}}+\int\frac{dk}{2\pi}\,\hat\beta(0,k)\hat h(-k)\hat h(k), \tag{44}$$

where we have chosen the charge on side 2 to be positive and used the expression for the area of a weakly modulated surface:

$$A_{\mathrm{real}}=\int dx\left(1+\frac{1}{2}h_x^2(x)\right)=\int dx+\int\frac{dk}{2\pi}k^2\hat h(-k)\hat h(k). \tag{45}$$

Of course the charge can also be obtained directly by integrating Eq. (10) over the real surface. It is important to note that $\hat{\beta}(0,k)$ depends on $\hat{\alpha}(k)$ and σ. Therefore, even if the terms linear in $h(x)$ are averaged out by integration, they have an influence on the second-order terms and must be taken into account. On the other hand, if we take into account only the nonlocal linear response of the dielectric displacement at the surface, we obtain the trivial result that $Q=\sigma A_{\mathrm{real}}$. This shows that it is crucial to go beyond the linear response of the dielectric displacement.

If we substitute Eq. (24) into Eq. (44), we get the expression for the capacity

$$C=AC_{GC}\tilde{R}(\kappa_i,\epsilon_i), \tag{46}$$

where A is the corresponding area of a flat surface and $\tilde{R}(\kappa_i,\epsilon_i)$ is given by

$$\tilde{R}(\kappa_i,\epsilon_i)=\frac{A_{\mathrm{real}}}{A}+\frac{h^2}{C_{GC}\Delta V}\int\frac{dk}{2\pi}\hat{\beta}(0,k)\hat{g}(k). \tag{47}$$

Here we have also defined the two-point height-height correlation function of the interface

$$\hat{g}(k)\equiv\frac{\hat{h}(-k)\hat{h}(k)}{Ah^2}, \tag{48}$$

where h is the height of the interface modulation $h(x)$. According to Daikhin *et al.* [16], the function $\tilde{R}(\kappa_i,\epsilon_i)$ is called the *roughness function* because it can be calculated from experimental data of the ratio C/AC_{GC} in order to get information about the roughness of the interface. Since the response function $\hat{\beta}(0,k)$ itself depends also on $C_{GC}\Delta V$ and contains a contribution $1-A_{\mathrm{real}}/A$ we can write the roughness function more conveniently as

$$\begin{aligned}\tilde{R}(\kappa_i,\epsilon_i)={}&1+h^2C_{GC}\int\frac{dk}{2\pi}\hat{g}(k)\\&\times\left\{\frac{\kappa_1}{\epsilon_1}\left(1-\frac{1}{r_{1,k}}\right)+\frac{\kappa_2}{\epsilon_2}\left(1-\frac{1}{r_{2,k}}\right)+C_{GC,k}\right.\\&\left.\times\left[\frac{1}{\epsilon_2}\left(1-\frac{1}{r_{2,k}}\right)-\frac{1}{\epsilon_1}\left(1-\frac{1}{r_{1,k}}\right)\right]^2\right\}.\end{aligned} \tag{49}$$

This shows that the capacity for ITIES with a modulated interface is always greater than the Gouy-Chapman capacity since $\tilde{R}(\kappa_i,\epsilon_i)\geqslant 1$. The roughness function determines the deviation of the capacity from the Gouy-Chapman prediction in terms of the height-height correlation function and describes the interplay between the different length scales of the system. This is a quite general result and it can be applied also to semiconductor-metal, semiconductor-electrolyte, and metal-electrolyte interfaces. The roughness function for an ideal metal-solution interface, for example, can be easily obtained from Eq. (49) by performing the limit $\epsilon_2\to\infty$, $\kappa_2\to\infty$. In this case the roughness function reduces to

$$\tilde{R}(\kappa_1,\epsilon_1)=1+\kappa_1^2h^2\int\frac{dk}{2\pi}\hat{g}(k)(r_{1,k}-1), \tag{50}$$

which is exactly the result obtained by Daikhin *et al.* [16], who started from an equipotential line as boundary condition. For all other cases, especially for semiconductor-electrolyte interfaces where the charge carrier concentration on both sides is low, one should apply Eq. (49) instead of Eq. (50).

Besides the information about the surface via the height-height correlation function $\hat{g}(k)$, the function $\tilde{R}(\kappa_i,\epsilon_i)$ has another important consequence. The Gouy-Chapman capacity for liquid-liquid interfaces can simply be written as a series combination of the two independent diffuse layer capacities on sides 1 and 2 [see Eq. (25)]. This is no longer true if the interface deviates from a planar geometry since the response function $\hat{\beta}(0,k)$ introduces a coupling between the two diffuse layer capacities. This shows that even on the mean field level we have a coupling between the two diffuse layers, which vanishes for $h=0$. In other words, the absence of the coupling in the Gouy-Chapman theory is due to the symmetry of the interface, but generally this symmetry is broken and the two diffuse layers are not independent of each other.

For a better understanding of this coupling we consider the special case of $\kappa_1=\kappa_2=\kappa$. In this case the roughness function decouples into two parts, one of which is independent of the dielectric constants

$$\begin{aligned}\tilde{R}(\kappa,\epsilon_1,\epsilon_2)={}&1+\kappa^2h^2\int\frac{dk}{2\pi}\hat{g}(k)\left(1-\frac{1}{r_k}\right)\\&\times\left\{1+(r_k-1)\left(\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\right)^2\right\}.\end{aligned} \tag{51}$$

We can simplify this expression further if we make another approximation. Assume that the height function has a smallest correlation length l_{min} and that the Debye length is much smaller than l_{min}, i.e., $\kappa l_{\mathrm{min}}\gg 1$. In this limit we can expand the quantity r_k, which yields

$$\tilde{R}(\kappa,\epsilon_1,\epsilon_2)=\frac{A_{\mathrm{real}}}{A}-\frac{3}{8}\frac{\langle H^2\rangle}{\kappa^2}+\frac{1}{4}\frac{\langle H^2\rangle}{\kappa^2}\left(\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\right)^2, \tag{52}$$

with the mean squared curvature $\langle H^2\rangle$ of the interface

$$\langle H^2\rangle=\int\frac{dk}{2\pi}k^4h^2\hat{g}(k)=\frac{1}{A}\int dx\, h_{xx}^2(x). \tag{53}$$

Equation (52) can be interpreted in the following way: Instead of representing the Gouy-Chapman capacity as a series combination of two plate capacitors, in our case it is more convenient to represent it as only one plate capacitor with two different dielectric media in between. This type of capacitor can also be described by Eq. (25). The average thickness of one sort of dielectric is given by $1/\kappa_i$ and the boundary between is just described by the height function $h(x)$. Then the terms independent of ϵ in Eq. (52) simply take into account the deviation of the two capacitor plates from a planar geometry. The farther the plates are from the modulated interface, the flatter they are because the diffuse layer ''smears'' out the modulation of the interface; hence the sum of these terms becomes smaller. In addition there is a coupling due to the difference of the dielectric media. This coupling increases with increasing ratio of $\langle H^2\rangle/\kappa^2$ or $\lambda_{DB}^2/\langle R^2\rangle$, where R is the curvature radius. For a small curvature radius the electric field in the diffuse double layer, which is a function of both dielectric constants, is very inhomogeneous with respect to the lateral dimension. If, however, the Debye length is smaller than the curvature radius, this inhomogeneity effect is much lower since the electric field is already considerable screened. It vanishes also for equal dielectric constants because then this effect is equal but opposite on both sides of the interface. In the general case of $\kappa_1 \neq \kappa_2$, both these effects are coupled together and the behavior is too complicated to represent in a simple picture.

Before we calculate the roughness function for a specific example, it is illustrative to investigate two extreme limiting cases: If the height function has a smallest correlation length $l_{\min}$, then the quantity $r_{2,k}$ has the limit

$$\lim_{\kappa_2\to\infty} r_{2,k}=1. \tag{54}$$

The roughness function [Eq. (49)] is now completely determined by the Debye length of side 1 and it is the same as for the metal-solution interface [Eq. (50)]. This is of course expected since at this level of description, the screening on side 2 is now perfect, like for an ideal metal. If we further assume that $\kappa_1 l_{\min} \gg 1$, we can develop the quantity $r_{1,k}$ and the roughness function can be approximated by

$$\tilde{R}(\kappa_1)=\frac{A_{\text{real}}}{A}-\frac{1}{8}\frac{\langle H^2\rangle}{\kappa_1^2}. \tag{55}$$

In this limit the roughness function is determined by the ratio of the curvature and the inverse Debye length. Equations (54) and (55) show that the geometrical roughness of the interface is accessible by capacity measurements only in the limit of zero Debye length on *both* sides, since then both diffuse layers follow exactly the modulation of the interface. On the other hand, if only *one* Debye length goes to infinity, one recovers the Gouy-Chapman capacity.

In order to investigate the behavior of the roughness function over the complete range of the Debye lengths on both sides, we assume that the modulation function $h(x)$ can be described by a simple deterministic function

$$h(x)=h\cos\frac{2\pi}{\lambda}x,\quad \hat{h}(k)=\frac{hA(\delta_{m,1}+\delta_{m,-1})}{2}, \tag{56}$$

where $k=2\pi m/\lambda$ and $m=0,\pm 1,\pm 2,\ldots$. The integral $\int dk/2\pi$ in Eq. (49) can then be replaced by the summation $(1/A)\Sigma_k$ and the roughness function is simply given by

$$\tilde{R}(\kappa_i,\epsilon_i)=1+\frac{1}{2}h^2\left\{C_{GC}\frac{\kappa_1}{\epsilon_1}\left(1-\frac{1}{r_{1,p}}\right)+\frac{\kappa_2}{\epsilon_2}\left(1-\frac{1}{r_{2,p}}\right)+C_{GC,p}\left[\frac{1}{\epsilon_2}\left(1-\frac{1}{r_{2,p}}\right)-\frac{1}{\epsilon_1}\left(1-\frac{1}{r_{1,p}}\right)\right]^2\right\}. \tag{57}$$

A three-dimensional plot of this function is shown in Fig. 1. It can be clearly seen that the roughness function reaches the geometrical roughness only for the case $\kappa_1 h=\kappa_2 h\to\infty$.

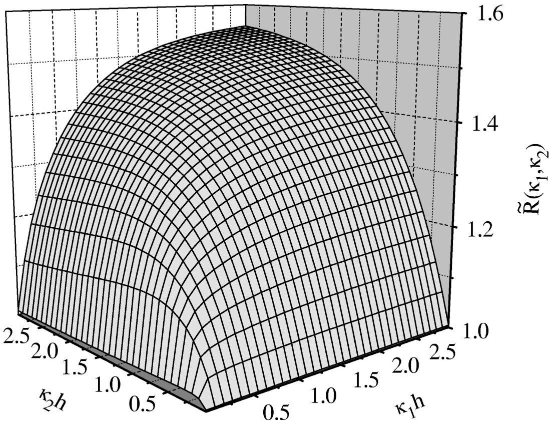

FIG. 1. Roughness function for a periodic interface [Eq. (57)] with $h=6$ Å, $\lambda=24$ Å, $\epsilon_1=80$, and $\epsilon_2=10$. The geometrical roughness A_{real}/A is 1.62.

However, as discussed above, if the concentration on one side is zero, the roughness function is one. Furthermore, it is seen that the roughness function is close to the limiting value far before $\kappa h \gg 1$. Hence the approximation made for the perturbative calculation of the potential is valid over the whole interesting range. The roughness function is also not symmetric with respect to the line $\kappa_1 h=\kappa_2 h$. This is due to the difference of the dielectric constants; the greater this difference, the greater the asymmetry. Another interesting effect is the following: If the inverse Debye length on the side with the higher dielectric constant is small and fixed (κ_1 small), the roughness function is nonmonotonic with respect to κ_2. Unfortunately, in experimental investigations of ITIES the concentrations of the two electrolytes are usually changed symmetrically; therefore, this type of behavior cannot be observed.

In Fig. 2 we compare the roughness function for various differences of the two dielectric constants and $\kappa_1=\kappa_2$. This figure shows that the roughness, as seen in the capacity data, is the more pronounced the greater the difference of the dielectric constants. In the small κ limit the roughness function decays more smoothly to one, when the difference of the dielectric constants is small. Note that the upper curve corresponds also to the roughness function of a metal-solution interface [Eq. (50)].

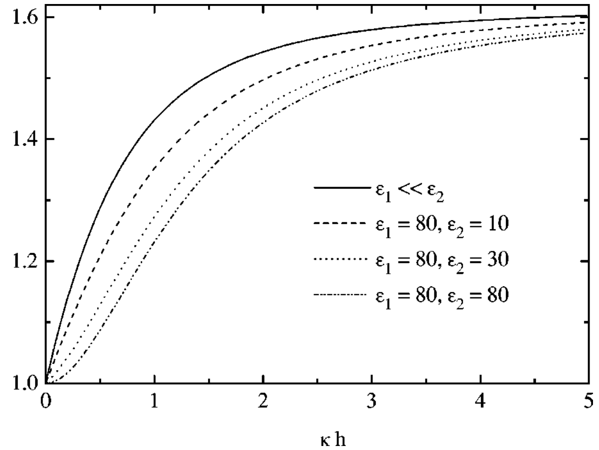

FIG. 2. Roughness function for a periodic interface [Eq. (57)] for different values of ϵ_1 and ϵ_2, with $h=5$ Å and $\lambda=20$ Å.

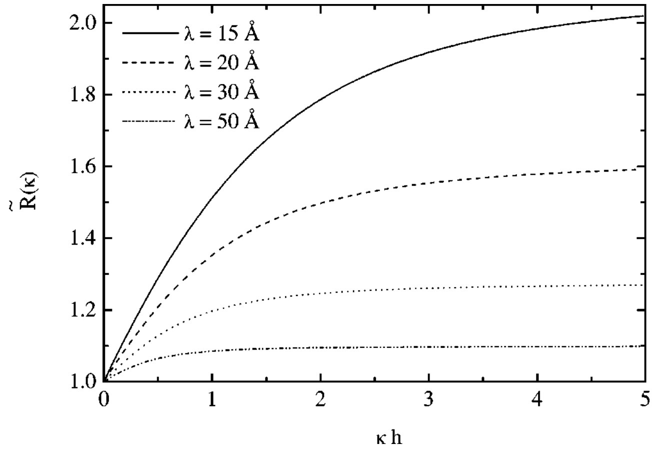

FIG. 3. Roughness function for a periodic interface [Eq. (57)] for different values of λ, with $h = 5$ Å, $\epsilon_1 = 80$, and $\epsilon_2 = 10$.

Figure 3 finally compares the roughness function for different parameters of h and λ. For a large value of h/λ the capacity of a modulated ITIES can be considerable higher than the result predicted by the Gouy-Chapman theory. These values are in agreement with experimental findings [5]. In [5] the higher capacity was explained by the existence of a mixed solvent region, including the ions, which results in an overlapping of the two space charge regions. Our results are not in contradiction with this. Indeed, we can argue in a similar way, because an averaging over the lateral direction of the ionic density profiles appears also as an ‘‘overlapping’’ if one considers the midplane of the interface at $y = 0$.

IV. FREE ENERGY AND BENDING MODULUS

The externally controlled variable for an ideally polarizable ITIES is the total potential drop ΔV across the interface. Therefore, we have to calculate the free energy in terms of ΔV, which is most easily done by starting from the Lippmann equation [21]

$$\left(\frac{\partial \gamma}{\partial(\Delta V)}\right)_{\mu_1,\mu_2} = -\frac{Q}{A_{\mathrm{real}}}. \tag{58}$$

Integration on both sides leads to the expression

$$A_{\mathrm{real}}(\gamma - \gamma_0) = \Delta F = -\int_0^{\Delta V} Q(\Delta V')\, d(\Delta V'). \tag{59}$$

Here γ_0 is the surface tension in the absence of a potential drop and ΔF is the change in free energy due to the formation of the diffuse double layers. Expressing Q through the capacity from Eq. (46) simply yields

$$\frac{\Delta F}{A} = -\frac{1}{2} C_{GC} (\Delta V)^2 \tilde{R}(\kappa_i, \epsilon_i). \tag{60}$$

This shows that also the free energy of a modulated ITIES is determined by the behavior of the roughness function.

As mentioned in the Introduction, liquid-liquid interfaces can serve as a model for biological membranes, which often have a very low surface tension. The modulation of the membranes is then mostly governed by the elastic bending modulus k_c. These membranes are usually immersed into electrolytes and it is therefore important to know the electrostatic contribution to the bending modulus. Since k_c has the dimensions of energy, the electrostatic contribution to it must have the form $f\epsilon(\Delta V)^2/\kappa$ or $f\sigma_0^2/\epsilon\kappa^3$ for a constant surface charge. Here f is a dimensionless constant that is determined by the boundary condition. The exact value and the sign of f are important since k_c enters, for example, exponentially the persistence length [23], which is a measure for the distance over which the normals of the surface become decorrelated, and it can be measured with great precision [24]. Phenomenologically, the total free energy of a two-dimensional modulated surface can be written as [13,18]

$$F_{\mathrm{surf}} = \gamma_0 \int dS + k_c \int dS (H - c_0)^2 + \tilde{k} \int dS\, K, \tag{61}$$

where c_0 is the spontaneous curvature and $\tilde{k}$ the Gaussian bending modulus. The mean curvature H and the Gaussian curvature K are given by

$$H = \mathrm{div}\left(\frac{\nabla h(x,y)}{\sqrt{1 + [\nabla h(x,y)]^2}}\right),$$

$$K = \frac{h_{xx} h_{yy} - h_{xy}^2}{\sqrt{1 + [\nabla h(x,y)]^2}},$$

and the metric dS is

$$dS = \frac{dx\,dy}{\sqrt{1 + [\nabla h(x,y)]^2}}. \tag{62}$$

For a one-dimensional and only weakly modulated surface with zero spontaneous curvature this expression simplifies to

$$F_{\mathrm{surf}} = \gamma_0 \int dx \left(1 + \frac{1}{2} h_x^2(x)\right) + \frac{1}{2} k_c \int dx\, h_{xx}^2(x). \tag{63}$$

Using again the limit $\kappa l_{\min} \gg 1$ and assuming equal Debye lengths for simplicity, we can expand the roughness function and write the free energy [Eq. (59)] in this limit as:

$$\begin{aligned} F = {} & \left[\gamma_0 - \frac{1}{2}\left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}\right) \kappa (\Delta V)^2\right] \int dx \left(1 + \frac{1}{2} h_x^2(x)\right) \\ & + \frac{1}{16}\left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}\right) \frac{(\Delta V)^2}{\kappa} \left[3 - 2\left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}\right)^2\right] \int dx\, h_{xx}^2(x). \end{aligned} \tag{64}$$

If we compare this expression for the free energy with the coefficients of the expression in Eq. (63), we can identify $-\epsilon_1 \epsilon_2 \kappa (\Delta V)^2 / 2(\epsilon_1 + \epsilon_2)$ as the electrostatic contribution to the surface tension. The electrostatic contribution to the bending modulus is then given by

$$k_c(\Delta V) = \frac{1}{8}\left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}\right) \frac{(\Delta V)^2}{\kappa} \left[3 - 2\left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}\right)^2\right]. \tag{65}$$

In the limit $\epsilon_2 \gg \epsilon_1$ this expression reduces to

$$k_c(\Delta V)=\frac{1}{8}\frac{\epsilon_1(\Delta V)^2}{\kappa}, \tag{66}$$

where ΔV is now the equipotential at the surface [see Eq. (38)]. This is just the result obtained previously by several authors using different approaches [15,22,25,26]. Note that we obtain this result also in the limit $\kappa_2 \gg \kappa_1$. In both cases the electrostatic contribution to the bending modulus is controlled by that side, in which most of the potential drop occurs, since on the other side the electric field is extremely shielded. If instead the potential drop occurs on both sides, the full equation (65) should be applied. In the special case of $\epsilon_1=\epsilon_2$ we obtain

$$k_c(\Delta V)=\frac{3}{16}\frac{\epsilon(\Delta V)^2}{\kappa}. \tag{67}$$

This result differs from that obtained by other authors [25,26], who considered the curvature energy of a charged membrane with electrolytes on both sides. They obtained a value of $k_c(V_0)=\epsilon V_0^2/4\kappa$ for a perfectly conducting membrane with an equipotential line V_0 at the boundary. In our case ΔV is the total potential drop across the interface and the potential at the interface is not constant [see Eq. (35)].

Often the membrane carries a constant surface charge due to charged groups in the molecules that constitute the membrane. The electrolyte contains then also the counterions of these charged groups. We can model this effect if we assume that the total charge on side 1 consists of a constant singular part σ_0 and the diffuse part. In this case we have to write the boundary condition Eq. (9) as

$$\mathbf{n}(x)[\mathbf{D}_1(x,y=h(x))-\mathbf{D}_2(x,y=h(x))]=\sigma_0. \tag{68}$$

If we perform the same type of calculation as described in Sec. II, we obtain in the special case of $\kappa_2=\kappa_1$ for the total charge Q the expression

$$\frac{Q}{A}=\Delta V C_{GC}\tilde{R}(\kappa,\epsilon_1,\epsilon_2)-\sigma_0 C_{GC}\frac{A_{\rm real}}{A}\left(\frac{1}{\epsilon_1\kappa}+R_{\sigma_0}(\kappa,\epsilon_1,\epsilon_2)\right), \tag{69}$$

with

$$R_{\sigma_0}(\kappa_i,\epsilon_i)=\kappa h^2\int\frac{dk}{2\pi}\hat{g}(k)(1-r_k)\times\left(\frac{1}{r_k}-1\right)\frac{1}{\epsilon_1+\epsilon_2}\left(\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\right). \tag{70}$$

If we now substitute Eq. (69) into the Lippmann equation and proceed in the same way as before, we obtain an additional contribution to the bending modulus

$$k_c=k_c(\Delta V)+k_c^{\sigma_0}(\Delta V,\sigma_0), \tag{71}$$

with

$$k_c^{\sigma_0}(\Delta V,\sigma_0)=\frac{\Delta V\sigma_0}{\kappa^2}\frac{\epsilon_1\epsilon_2}{(\epsilon_1+\epsilon_2)^2}\left(\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\right). \tag{72}$$

Note that this contribution is asymmetrical in ΔV, σ_0, and $\epsilon_1-\epsilon_2$. Furthermore, it vanishes for $\epsilon_1=\epsilon_2$. If, for example, $\Delta V\sigma_0>0$ and $\epsilon_1<\epsilon_2$, then the contribution to the bending modulus is negative and the interface is destabilized. Due to the second term in Eq. (69) we obtain a potential of zero charge if $Q=0$. The zeroth order of this potential of zero charge is just $\Delta V_{pzc}^{(0)}=\sigma_0/\epsilon\kappa$. Since the terms proportional to the bending modulus give already a second-order contribution to the free energy, we can calculate the bending modulus for $\Delta V=\Delta V_{pzc}^{(0)}$ and obtain in the special case of $\epsilon_1=\epsilon_2$

$$k_c(\sigma_0)=\frac{3}{16}\frac{\sigma_0^2}{\epsilon\kappa^3}. \tag{73}$$

This result is three times greater than that obtained in [25,26]. So the response of the dielectric displacement at the interface to the curvature leads to a stabilization of the flat interface compared to the case with a constant dielectric displacement at the interface.

V. CONCLUSION

In this work we have developed an extension to the linear Gouy-Chapman theory, which takes into account a modulation of the interface position. Special emphasis was given to the boundary condition for a liquid-liquid interface. The appropriate boundary condition fixes neither the potential nor the surface charge at the interface position. Instead, the dielectric displacement at the boundary was allowed to vary in the lateral direction. This variation is due to a nonlocal and nonlinear response of the dielectric displacement to the perturbation from a flat interface geometry.

Within this model it was shown that the capacity of an interface between two immiscible electrolyte solutions can be significantly higher than the value predicted by the Gouy-Chapman theory. The deviation depends on the interplay between the Debye lengths of the two solutions and the height and characteristic length of the interface modulation. This interplay is described by a roughness function, which governs also the free energy of the system. Since the roughness function is just the ratio of the ‘‘real’’ capacity to the Gouy-Chapman capacity, it can be measured very easily. If the roughness function is known for various concentrations, one can get information about the height-height correlation function of the interface.

Furthermore, we calculated the electrostatic contribution to the elastic bending modulus, which determines the curvature fluctuations of the interface. Our result is different from previous ones since we have employed a different boundary condition.

The model we used in this work to describe the liquid-liquid interface between to immiscible electrolyte solutions is of course idealized. Thus it neglects the effect of specific ion adsorption or interfacial ion association, but from experimental investigations of liquid-liquid interfaces it is well known that theses effects play an important role. In future work we will incorporate these effects into our model.

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